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Unusual Edge Shift of Stepwise-Reduced Cobalt Tetraphenylporphyrin and Tetrabutylphthalocyanine

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Introduction: We have shown that metallo-porphyrins and phthalocyanines (M = Co and Fe) are effective photocatalysts in the reduction of CO_2 to CO and formate [1-3]. Metal(I) tetraphenylporphyrins ($M^{I}TPP$) and metal(I) tetrabutylphthalocyanines ($M^{I}TBPc$) do not react with CO_2 until they are reduced beyond the M(I) state. The site of reduction, metal *versus* macrocycle, along with changes in the catalyst's structural and electronic properties are important in understanding the active species in these catalytic reactions. Therefore we have recently measured the XANES of a series of CoTPP and CoTBPc.

Methods and Materials: Stepwise reduction of $Co^{II}TPP$ and $Co^{II}TBPc$ were carried out in CH_3CN using Na-Hg in homemade cells. The purity of these air-sensitive samples was examined by measuring optical spectra before and after the XANES measurements. The decomposition of samples is typically much less than 10 %. XANES of $[Co^{III}TPP(Cl)]$ and $[Co^{III}TPP(py)_2]^+$ (py = pyridine) were also measured.

Results: XANES results of CoTPP and CoTBPc are shown in Figures 1 and 2, respectively. In $Co^{III}TPP^+$, the chloride ion donates more electron density to the cobalt(III) center than pyridine, and partially reduces the metal, resulting in a –1 eV edge shift. It is striking that XANES spectra for $Co^{II}TPP$, $[Co^{I}TPP]^-$, and $[Co^{0}TPP]^{2-}$ exhibit no main-edge shift. However the pre-edge ($1s \rightarrow 4p_z$) positions for $Co^{II}TPP$, $[Co^{I}TPP]^-$, and $[Co^{0}TPP]^{2-}$ are sensitive to stepwise reduction. The main-edges for $Co^{II}TBPc$, $[Co^{I}TBPc]^-$, $[Co^{I}TBPc^{\bullet-}]^{2-}$ and $[Co^{0}TBPc^{\bullet-}]^{3-}$ also indicate no shift, however, the pre-edges are sensitive to the oxidation state of the cobalt centers (see Figure 2). The lack of edge shifts upon reduction of $Co^{II}TPP$ and $Co^{II}TBPc$ suggests that considerable electron density resides in the ligand π system. However, the pre-edge shifts are consistent with the assignments from the optical spectra. In the case of CoTPP, the first and second reductions of $Co^{II}TPP$ are metal-centered to form $[Co^{I}TPP]^-$ and $[Co^{0}TPP]^{2-}$, respectively. In the case of cobalt phthalocyanines, the first, second and third reductions of $Co^{II}TBPc$ are metal-, ligand- and metal-centered reductions, respectively, forming $[Co^{I}TBPc]^-$, $[Co^{I}TBPc^{\bullet-}]^{2-}$ and $[Co^{0}TBPc^{\bullet-}]^{3-}$. Origin of pre-edge shift and doubling of the $1s \rightarrow 4p_z$ edge (in Co(I) and Co(0) species) are under investigation.

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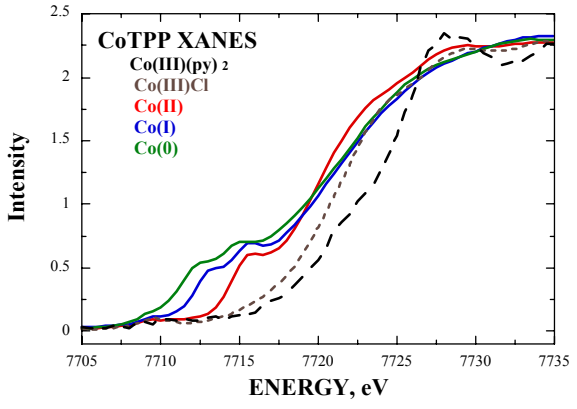

Figure 1. XANES of CoTPP

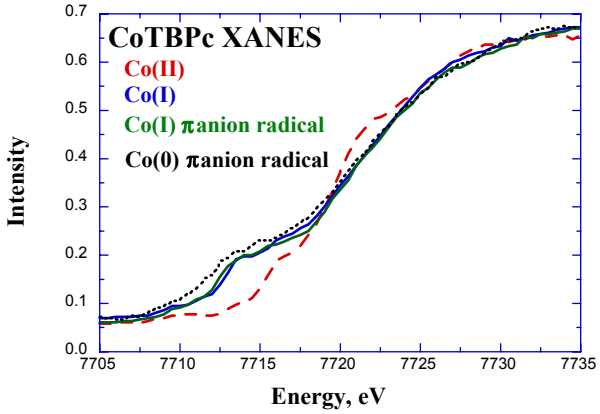

Figure 2. XANES of CoTBPc